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RF Sputtered Transparent Conductors The System In_2O_3 - SnO_2

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Abstract—An rf sputtering technique for the deposition of tin-doped indium oxide transparent conductors has been developed. The technique employs the creation of anion vacancies in the films in addition to donor doping by tin oxide. Films as deposited exhibit transmission in the visible, averaging 90% or higher for sheet resistivities greater than 15 ohms/square. Upon annealing at 550°C in air for two hours, the resistivity increases by a factor of 2–7, depending upon the initial resistivity, but the average transmission remains unchanged. The resistivity change is a result of surface oxidation that eliminates some of the anion vacancies created during deposition. The films are fine grained, smooth polycrystals. Dopants other than Sn yield higher resistivity and lower optical transmission.

Introduction

Previously, rf sputtered transparent conductors in the system SnO_2 - Sb_2O_3 were reported¹ to yield transmission greater than 80% in the visible range of wavelengths for films having sheet resistivities greater than 500 ohms per square. Conductivity was induced in the films by donor doping rather than by creating anion vacancies, because the latter was found to be less controllable.

For certain applications, the conductivity that can be achieved for a given transmission was found to be inadequate. Accordingly, a search was made to find a material system that provides greater conductivity than the SnO_2 - Sb_2O_3 system for equivalent transmission in the visible. Based on a variety of considerations, the material system selected for this investigation was In_2O_3 - SnO_2 .

Pure In_2O_3 films prepared by reactive dc sputtering² from an indium target yielded transmission of only 75% at a sheet resistivity of 1500 ohms/square. Sinclair, et al³ used In_2O_3 as an acceptor dopant in SnO_2 films and found the resistivity to be higher than for pure SnO_2 . However, their investigation included only small In_2O_3 additions

(up to 7 mole %). This paper covers the compositional range 10 to 50 mole % SnO_2 in In_2O_3 . In the present case, SnO_2 is a donor impurity in the In_2O_3 .

The oxidation is self-limiting⁴ in thickness at any given temperature. This effect suggests that anion vacancies can be created and maintained stably with this material, i.e., subsequent oxidation processes should tend to form a passivation layer on the top surface of the film, limiting further oxidation at lower temperatures.

Experimental Techniques

Sputtering targets were prepared by dry mixing reagent grade In_2O_3 and SnO_2 powders, pressing the powder into shallow nickel dishes that were pre-coated with a thick film of rhodium, which acts as a reaction barrier. The powders were then lightly sintered in air at 900°C for one hour. This method of target preparation has proven very useful when a wide range of compositions are to be investigated. It should be noted, however, that targets prepared in this fashion are extremely porous and require careful outgassing before each sputtering run to ensure that stable conditions prevail. These and other precautions to be observed with these targets have been described.¹

The sputtering equipment has been described previously.⁵ In operation, shields are placed close to the target to prevent sputtering any exposed rhodium or nickel from the dish.

To determine the optimum target composition, films were deposited to a thickness of 1200 Å in pure oxygen. These runs yielded films with a minimum of anion vacancies and are taken to be the stable condition of the material. All films were deposited under the following sputtering conditions:

Oxygen Pressure: 40 millitorr
Peak-to-Peak rf Voltage: 4300 volts
Average Sheath Potential: -800 volts
Magnetic Flux Density: 25 gauss
Target-Substrate Separation: 2.7 cm

Under these conditions, the deposition rate was 40 ± 2 Å/min. Fig. 1 shows the variation of sheet resistivity as a function of target composition for these films. At the minimum in the resistivity curve (20 mole % SnO_2), the sheet resistivity of 3,000 ohms/square is higher than an equivalently thick 90 SnO_2 -10 Sb_2O_3 by a factor of two.¹ From the data in Fig. 1, the composition selected for further study was 80 mole % In_2O_3 -20 mole % SnO_2 . All data following are for that composition.

To produce anion vacancies in the films, pure argon was used as the sputtering gas. It is known that both In_2O_3 and SnO_2 are chemically reduced partially when sputtered in argon.⁵ Unless otherwise indicated, all sputtering runs in argon were conducted under the following conditions:

Argon Pressure: 30 millitorr

Peak-to-Peak rf Voltage: 4300 volts

Average Sheath Potential: -850 volts

Magnetic Flux Density: 25 gauss

Target-Substrate Separation: 2.7 cm

The deposition rate was 150 ± 5 Å/min. These conditions were used for convenience only. It was found possible to deposit this material at rates up to about 700-750 Å/min without recrystallization or excessive grain growth.

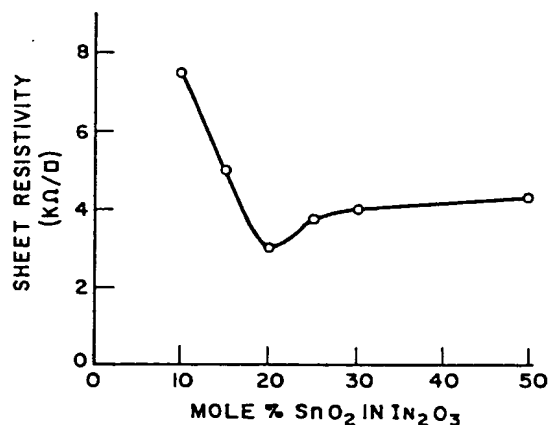


Fig. 1—Sheet resistivity versus target composition for 1000-Å-thick films deposited in pure oxygen.

Results and Discussion

Resistivity and Transmission

Fig. 2 illustrates the variation in transmission with wavelength and sheet resistivity of films as deposited. Figs. 3 and 4 show the effect on resistivity and transmission of annealing the films at 550°C for two hours in air. In all cases, the effect on transmission is to shift the peaks in Fig. 2 to lower wavelengths, but the average transmission over the visible range of wavelengths remains essentially unchanged. The curves are essentially interference patterns, and the wavelength

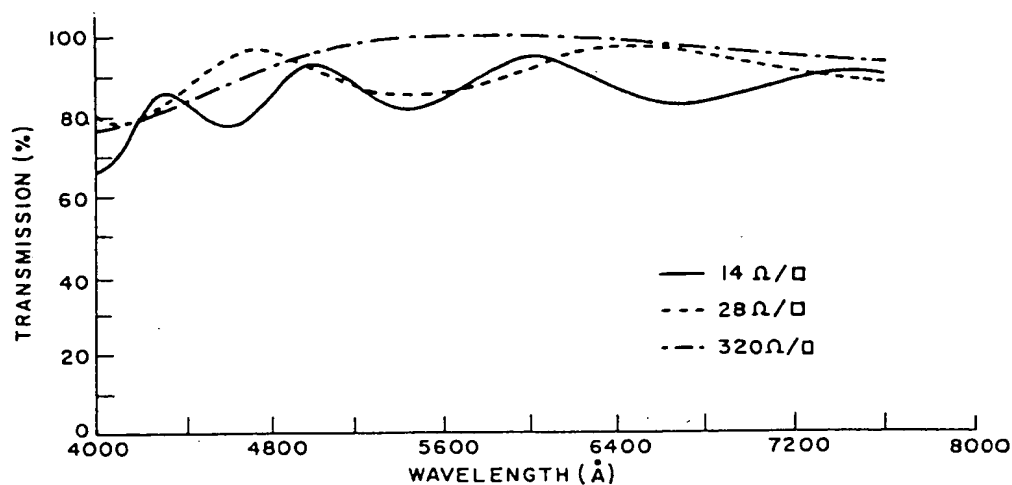


Fig. 2—Transmission versus wavelength for $\text{In}_2\text{O}_3\text{-SnO}_2$ films deposited in argon to different thicknesses.

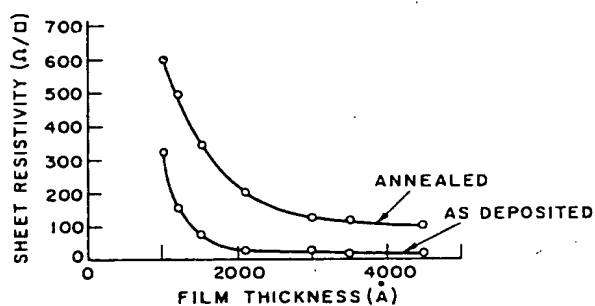


Fig. 3—Sheet resistivity versus film thickness for as-deposited and annealed $\text{In}_2\text{O}_3\text{-SnO}_2$ films.

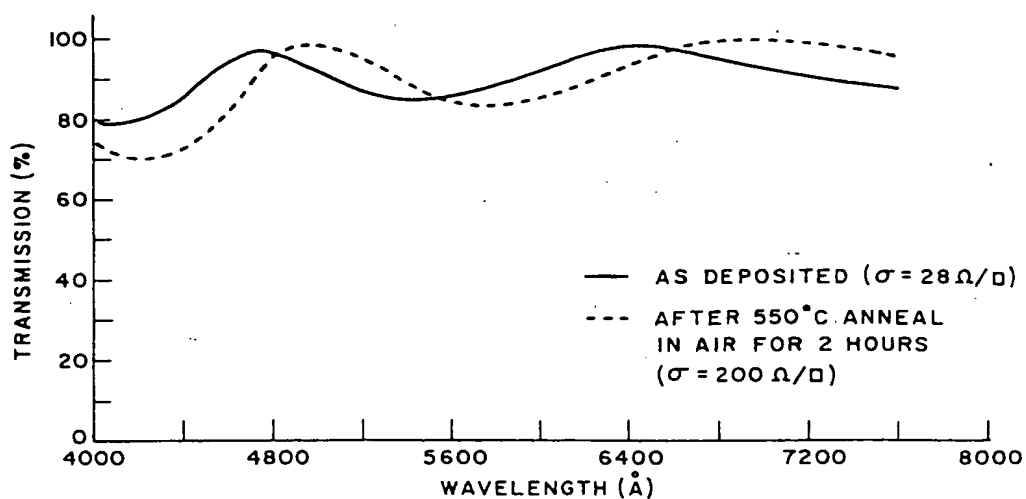


Fig. 4—Transmission versus wavelength for as-deposited and annealed $\text{In}_2\text{O}_3\text{-SnO}_2$ films.

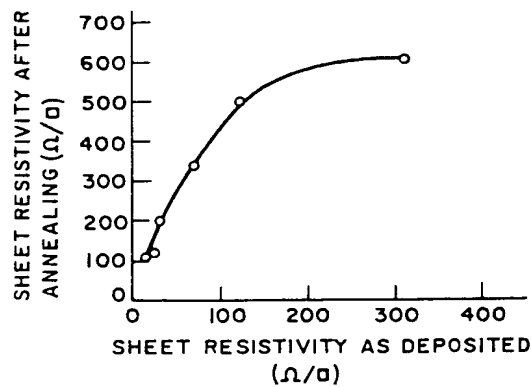


Fig. 5—Sheet resistivity after annealing versus sheet resistivity before annealing for $\text{In}_2\text{O}_3\text{-SnO}_2$.

shift implies a change in refractive index. For convenience, the annealed resistivity is plotted as a function of resistivity before annealing in Fig. 5.

For thickness greater than 2,000 Å, the bulk resistivity is constant ($625 \pm 5 \mu\text{ohm-cm}$ as deposited; $4,600 \pm 100 \mu\text{ohm-cm}$ after annealing). $\text{SnO}_2\text{-Sb}_2\text{O}_3$ films of comparable thickness exhibit resistivities 3 to 4 times higher than these values. Thinner films exhibit much higher bulk resistivities (Fig. 6). The thickness at which this departure from constant resistivity occurs is far greater than that for metal films. It should be noted that annealing these films does not cause their resistivity to increase to the values for films deposited in pure oxygen. This tends to support the view that a passivating surface oxide is grown on the film surface.

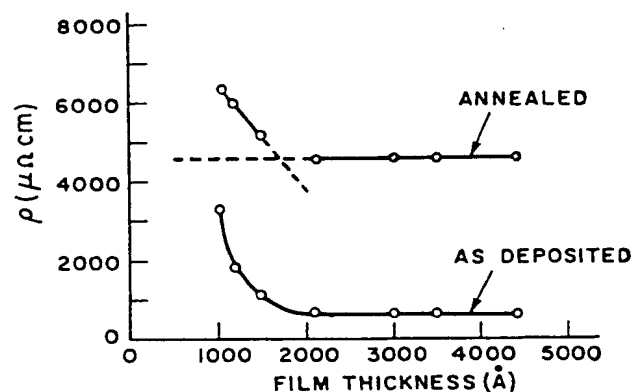


Fig. 6—Bulk resistivity versus film thickness for $\text{In}_2\text{O}_3\text{-SnO}_2$ as deposited and after annealing at 550°C for 2 hours.

Surface Morphology

The surface of the films produced by this technique are smooth when viewed in the scanning electron microscope (Fig. 7). There is no change in surface morphology after annealing at 550°C for two hours in air.

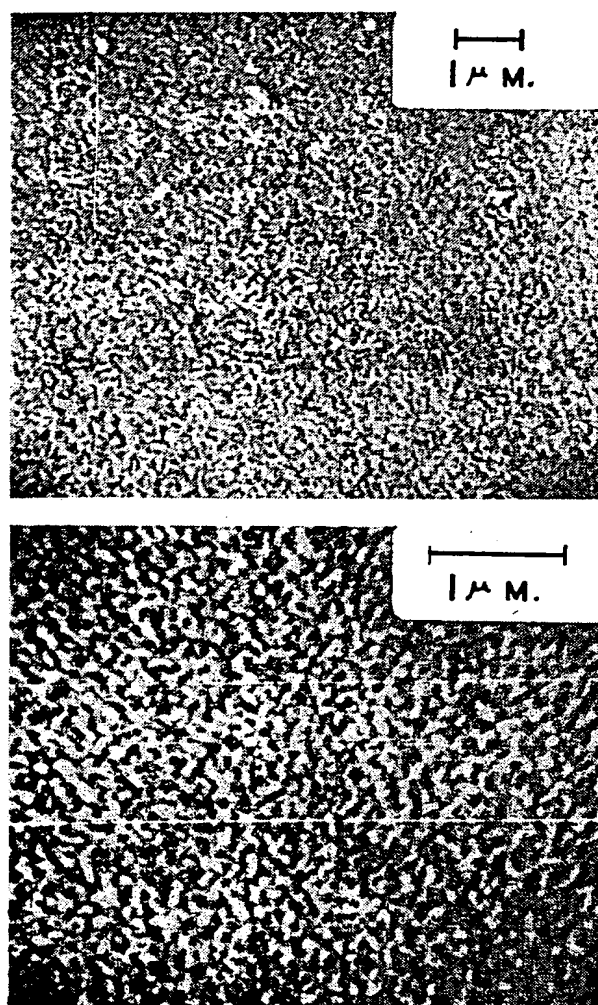


Fig. 7—Scanning electron micrographs of In₂O₃-SnO₂ ($t = 4000 \text{ \AA}$).

Crystal Structure

Electron diffraction analysis of films as deposited and after annealing reveal that the films are polycrystalline with a considerable amount of {100} preferred orientation (Fig. 8). The structure is cubic with a lattice parameter $a_o = 10.31 \text{ \AA}$ as compared to bulk In₂O₃ (a_o

$= 10.118$).⁶ No SnO_2 phases were detected, implying that the dopant replaces indium substitutionally in the In_2O_3 structure.

No difference between the annealed and as-deposited films was detected by electron diffraction.

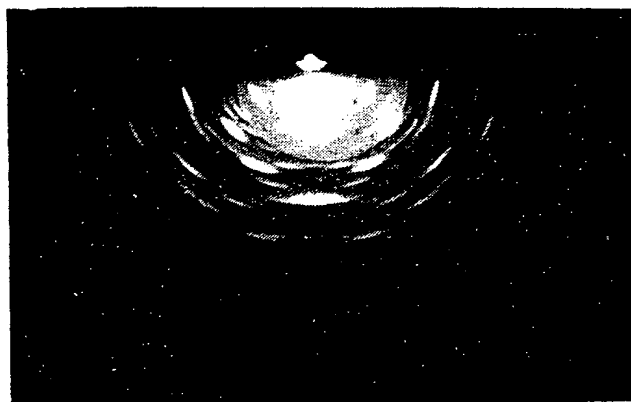


Fig. 8—Reflection electron-diffraction pattern of In_2O_3 - SnO_2 film.

Other Dopants in In_2O_3

Several other dopants were tried in In_2O_3 . None was found as effective as SnO_2 . Table 1 lists these dopants and the results obtained. Annealing these films again produced increases in resistivity with little or no change in transmission.

Table 1—Characteristics of Donor-Doped, Anion-Deficient In_2O_3 Films (Film Thickness = 2500 Å)

Dopant	Concentration (Mole %)	Resistivity (ohm-cm)	Average Transmission (%)
SnO_2	20	6.25×10^{-4}	93
Sb_2O_3	10	2×10^{-2}	88
Sb_2O_3	20	1.7×10^{-2}	85
Bi_2O_3	10	2×10^{-1}	5
PbO_2	20	4.5	23
TiO_2	20	7.5×10^{-1}	96

Conclusions

Transparent conductors in the material system In_2O_3 - SnO_2 exhibit minimum resistivity for equivalent transmission at a composition consisting of 80 mole % In_2O_3 -20 mole % SnO_2 . When rf sputtered in pure argon to produce anion vacancies, the films exhibit greater than

80% transmission in the visible for film resistivities greater than 15 ohms/square. Upon annealing the films in air at 550°C for two hours, the resistivity increases by a factor of 2 to 7 depending upon the initial resistivity; but the average transmission in the visible remains unchanged. The resistivity change is probably a result of surface oxidation that eliminates anion vacancies. Further annealing at or below 550°C produces no change in resistivity, leading to the conclusion that the oxide grown is self-passivating. The films are fine grained polycrystals and are smooth in texture.

Acknowledgments

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